

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 02-077494

(43)Date of publication of application : 16.03.1990

(51)Int.Cl.

C10M115/08
// C10N 30:00
C10N 40:02
C10N 50:10

(21)Application number : 63-228493

(71)Applicant : SHOWA SHELL SEKIYU KK
NIPPON SEIKO KK

(22)Date of filing : 14.09.1988

(72)Inventor : OZAKI KOYO
SHIMAKAWA YASUO
TANAKA KEIJI
NAKA MICHIHARU
KOIZUMI HIDEKI
SUZUKI TOSHIRO

(54) UREA GREASE COMPOSITION IMPROVED IN ACOUSTIC PERFORMANCE

(57)Abstract:

PURPOSE: To provide the title composition excellent in thermal stability and shear stability, small in softening tendency, improved in acoustic effect, containing each specific two kinds of diurea compound at specified ratio.

CONSTITUTION: The objective composition comprising (A) 90-20mol% of a compound of formula I (R1 and R3 are each 1-18C alkyl; R2 is bitolylene) and (B) 20-90mol% of a second compound of formula II (R4 and R6 are each 8C-saturated alkyl; R5 is diphenylmethane).

The preferable amount of this composition to be incorporated is 5-20 pts.wt. based on 100 pts.wt. of a mineral oil or synthetic oil.

R₁,NHCONHR₂,NHCONHR₃R₄,NHCONHR₅,NHCONHR₆

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

(57)

[WHAT IS CLAIMED IS:]

[Claim 1]

Thickener of grease; wherein; With compound 90 of the following nitramine (a) - with chemical agent 20 of 20 mol % and the following general formula (b) - 90 mol % is contained. Nitramine, (a) $R_1 \text{NHCONHR}_2 \text{NHCONHR}_3$ (b) $R_4 \text{NHCONHR}_5 \text{NHCONHR}_6$ (out of equation, R_2 shows linear of carbon number 18 or branch connection-shaped saturation alkyl group or unsaturated alkyl radical in bitoriren group, R_1 yo R_3 .) R_5 shows linear of carbon number 8 or divergence-shaped saturation alkyl group in diphenyl-methane group, R_4 and R_6).

[Claim 2]

Thickener of grease; wherein; It is from chemical agent 5 of 100 mixture part by weight and follows general formula containing with compound 90 of the following nitramine (a) - with chemical agent 20 of 20 mol % and the following general formula (b) - 90 mol % (c) - 90 part by weight. Nitramine, (a) $R_1 \text{NHCONHR}_2 \text{NHCONHR}_3$ (b) $R_4 \text{NHCONHR}_5 \text{NHCONHR}_6$ (c) $R_7 \text{NHCONHR}_8 \text{NHCONHR}_9$ (out of equation, as for R_2 , bitoriren group, R_1 show linear of carbon number 18 or divergence-shaped saturation alkyl group or unsaturated alkyl radical in yo R_3 .) R_5 shows linear of carbon number 8 or divergence-shaped saturation alkyl group in diphenyl-methane group, R_4 and R_6 . R_8 shows alkylation aromatic group or halogenation aromatic group in tolylene group or *bitoriren* group, R_7 and R_9).

[Claim 3]

Low sound urea grease composition of high drip-point; wherein; With grease thickener 2 of item the first claim or item the second - 30 part by weight is contained as against mineral oil or 100 synthetic oil part by weight.

[DETAILED DESCRIPTION OF THE INVENTION]

(a field of industrial application) the present invention relates to the high drip-point urea grease composition that sound ability is improved in particular. (the problems that prior art and invention are going to solve), in general terms, it became use as grease for thermostable at a wide point so that urea grease was compared with the grease which assumed lithium soap thickener, and drip-point could employ in high temperature in stable for heat for a long time highly. However, As for the ability of urea grease, only experience progressing year by year is slight, and there is much point number which, depending on the application, must be improved. By way of example only, When sound ability was watched, sound ability is extremely poor, and most of commercial urea grease are not usable in a point making much of sound ability at all. Therefore most of grease claiming to be for low sound are grease of lithium soap system. However, As claim such as small size of machine, lightweighting, precisely low soonka, life extension becomes high year by year, bearing used in these spin division in spite of being natural is small, and high speed rises to temperature so that spin or, besides, much accessories concentrate on high, it is in a severe situation in extremely for lubrication atmosphere. Many glees are examined to deal with these situation, but, there is not most of the grease satisfying all in ability side. By way of example only, As for the most of the thing bearing which a lot of, make much of sound ability that sound ability is comparatively good as for the grease of lithium soap system used as general-purpose grease broadly, this lithium soap system grease is used. However, Working temperature boundary cannot employ most in comparison with grease for thermostable (urea system, Cray system, complex soap system, sodic - tele cover ramet system) in the point where it is in high temperature low. On the other hand, Grease of urea system is superior in thermostability, is used willingly in a point becoming high temperature, but, sound ability is unsuitable for bearing making much of sound ability in extremely badly. In general, It is transferred a temporary swing by spin, and grease of minute amount or oil content is extremely supplied in sliding surface in spite of being repetition, and, as for the grease lubrication mechanism

in bearing, grease cut down in bearing lubricates churning, channeling in *chi* of. Sound detects vibration to occur in this sliding surface (between ball or koro and a race surface or retainer) as sound, but, there is the oscillation which solid foreign matter included within contaminated dirt and garbage and grease by external of the oscillation which bearing in itself of machine coming from *are* and *gata* of sliding surface has intervenes in bearing sliding surface as for this jolt, and occur. Solid debris included within grease is garbage, the dirt which are contaminated from so-called outside, but, the thickener which is grease medius decentralization imperfection is solid foreign matter of one, and sound ability is different in extremely by means of morphology and class of this thickener. By way of example only, Grease of lithium soap system gets the fiber structure which is steric by lithium hydroxide and oils and fats or saponification reaction with aliphatic acid, and gelation is done, but, fiber in itself can make good grease of sound ability in comparable easy it is small and and a *nan* silkworm and cooling method can do fiber by other treatment finely. In addition, In general terms, urea grease is grease containing compound comprising of reaction of ammine and isocyanate as thickener, but, most of urea chemical agent provided in this reaction are firm grain-shaped corpuscule, and these keep grease condition within oil dispersedly. If this grain-shaped grain is a big thing, because natural becomes bad sound ability, to some extent sound ability is improved by doing this corpuscule finely, but, of nature, is not improved. A thing and grain of thickener holding fiber structure are soft, and there is good grease in sound ability in urea grease, but, there is much grease which stability of machine is full of these, and wake up a poor thing or softening by heat or hardening. Additive such as succinic acid imide or metal salt abstergent is used so that is disclosed in prior art: by Japanese Patent Laid-Open No. 58-18593 (diurea system grease and the manufacturing process) and Japanese Patent Publication No. 62-44039 (high drip-point lithium complex grease composition), there are many cases improving sound ability by effect scattering thickener in uniformity. However, It is small, and, for the case urea grease in particular, most of the sound ability of nature cannot improve effect of these additive by the reason. Sound was efficient, and it tended to ignore a difficulty or sound ability to spread, besides, to produce superior grease in mechanical soundness and heat resistance. Say that it is the same urea grease urea grease can make extremely various kinds of grease by changing class of isocyanate and amine becoming charge stock of thickener or combination and and those ability branches out, and it is with character of otherwise terribly at all. (measure to solve a problem) as a result of bad shortcoming should have been overcome, and having studied the sound ability that conventional urea grease composition had inventors of application concerned zealously, much urea grease is produced experimentally, sound ability chooses particularly superior diurea chemical agent, when it made mix diurea chemical agent of each at the rate of specify, that sound ability, superior grease of shear stability were extremely provided was found. In other words, The grease which contained the thickener which made mix limited diurea compound at the rate of specify found a thing having superior ability in sound ability and shear stability. In other words, It is urea grease composition including what with grease thickener 2 of the first claims term or the second term - 30 part by weight contains as against grease thickener including it being from chemical agent 5 of 100 mixture part by weight and follows general formula containing with chemical agent 90 of grease thickener including the present invention containing with compound 90 of the following nitramine (a) - with chemical agent 20 of 20 mol % and follows general formula (b) - 90 mol % and follows general formula (a) - with chemical agent 20 of 20 mol % and follows general formula (b) - 90 mol % (c) - 90 part by weight and liquid petrolatum or 100 synthetic oil part by weight. Nitramine; (a) $R_1 NHCONHR_2$ $NHCONHR_3$ (b) $R_4 NHCONHR_5 NHCONHR_6$ (c) $R_7 NHCONHR_8 NHCONHR_9$

上式中、 R_2 はビトリレン基、 R_1 および R_3 は炭素数 18 の直鎖状または分枝状の、飽和アルキル基または不飽和アルキル基を示す。 R_5 はジフェニルメタン基、 R_4 および R_6 は炭素数 8 の直鎖状または分枝状の飽和アルキル基を示す。 R_8 はトリレン基もしくはビトリレン基、 R_7 および R_9 はアルキル置換芳香族基またはハロゲン置換芳香族基を示す。

Preferably when it made contain 5 - 20 part by weight as against mineral oil or 100 synthetic oil part by weight in the thickener, it is possible for grease of extremely superior ability. (a) And (b) sound ability does not improve when there is a little effect of blending application, and proportion 20 of compound goes over 90 mol % than mol % in diurea compost (b) when there is a little. (a) Thermostability is improved it is proportion 20 of compound - 90 mol % (a) and (b) when with chemical agent 5 - 90 part by weight was mixed for 100 mixture part by weight (c) for compound (b), drip-point improves. (c) When there is a more little proportion 5 of compound than part by weight, it is unfavorable from point of butterfly degree yield when effect of blending application is small, and 90 part by weight is gone over. When R_6 that diurea chemical agent and R_5 that R_3 that R_2 invited *bitoriren* radical, R_1 as for the grease by the present invention was linear of carbon number 18 or branching-shaped saturation alkyl group or unsaturated alkyl radical invited diphenyl-methane radical, R_4 mixed with the diurea chemical agent which was linear of carbon number 8 or branching-shaped saturation alkyl group or when R_9 that R_8 invited tolylene radical or *bitoriren* radical, R_7 added the diurea chemical agent which was alkylation aromatic group or halogenation aromatic group to the mixture, sound ability, shear stabilizer are diurea grease including a thing superior in extremely. It is provisional, $R_1 \dots R_9$ is converted to compound aside from superscription and diurea compound is made and is ineffective in in ability at all. By way of example only, R_1 and R_3 is octadecyl group, and stability of machine under high temperature of diurea grease is remarkable in the event of diphenyl-methane group and tolylene group, and R_2 is bad. In addition, As for the diurea grease which R_5 added thickener expressed in tolylene radical or *bitoriren* radical - diphenyl-methane radical to in R_4 and alkyl group of diurea grease and carbon number 10 which R_5 added thickener expressed in tolylene group or *bitoriren* group to with R_6 carbon number 8 - 14, stability of machine in high temperature is bad. As for R_7 more and the diurea grease which R_9 is alkylation aromatic group or halogenation aromatic group, and R_8 added thickener expressed in diphenyl-methane group to, sound ability is bad in extremely. R_1 and R_3 is octadecyl group, for example, and, for example, with chemical agent and R_4 that R_2 is expressed in *bitoriren* group (a) and R_6 is octyl radical, and, as for the grease by the present invention, R_5 improves stability of machine in the room temperature which is second in case of chemical agent isolated application because specify puts chemical agent expressed in diphenyl-methane radical (b) together, even more particularly, improvement of sound ability was measured. In addition, (a) And (b), even more particularly, compost of compound improves drip-point without, even more particularly, R_7 and R_9 losing ability of superscription because R_8 adds chemical agent expressed

in tolylene radical or *bitoriren* radical (c) in alkylation aromatic group or halogenation aromatic group, superior grease can improve in thermostability. Various additive such as oxidation inhibitor, extreme pressure agent and abrasion proof agent may be added to improve ability of this lubricating grease more. (an effect of the invention) even if, as for the diurea grease of the present invention, sound ability is remarkable, and thermostability before reaching high temperature, stability of machine are well done for a long time by high temperature, and a superior thing is done from the start by ordinary temperature, grease configuration is stable, and gravitation of softening by hardening or shear is small. In addition, Shear soundness before reaching high temperature from ordinary temperature is preferable, and demineralization gravitation is small extremely generally superior urea grease. As follows, Embodiment is advocated, and content of the present invention is explained. Base oil of 60 % by weight of 3,3 4,4 □CE - *bitoriren* - □CE - diisocyanate and all base oil quantity of compound is put in grease kettle in comparative example 1-3, blending ratio of coal shown in example 1 to 5 table 1 (a), and it heats to about 80 degrees Celsius, after having dissolved diisocyanate, it was drastic, and alkylamine of the chemical agent which made this dissolve in base oil of 20 % by weight of all base oil quantity (a) was stirred as well as gradual. After, about 10 minutes (b) later, having added 4,4 diphenyl-methane □CE - diisocyanate of compound, the octyl amine which made it was similar, and dissolve in base oil of 20 % by weight of quantity of *zen* base oil was added, and stirring was continued. The temperature rose by reaction of diisocyanate and amine, but, it made, in this state, 170 degrees Celsius were heated to after agitation, and conclude reaction for about 30 minutes. Afterwards, *ho* cold water was kneaded to room temperature, and grease was made. 11cst (100 degrees Celsius), the polyol ester oil were 7cst viscosity of mineral oil shown in embodiment (100 degrees Celsius). Resultant of butterfly degree (25 degrees Celsius, non-misce) and sound examination was shown in table 1 after a butterfly degree, drip-point of grease of each embodiment, shell roll (room and 150 degrees Celsius, 24h), heat in 150 degrees Celsius. Mineral oil of 80 % by weight of diisocyanate and all mineral oil quantity is put in grease kettle in comparative example 4-9, blending ratio of coal shown in 6-10 embodiment table 2s, it heats to about 80 degrees Celsius, after having made dissolve diisocyanate, the amine which made dissolve in liquid petrolatum of 20 % by weight of all liquid petrolatum quantity was added, and it was stirred. After, in this state, having continued a churn for about 30 minutes, it makes 170 degrees Celsius are heated to, and reaction conclude, *ho* cold water was kneaded in room temperature, and grease was made. Next, Diurea grease comprising of diurea grease and the (c) compound of example 3 was mixed; and grease was made. Resultant of butterfly degree (25 degrees Celsius, non-misce) and sound examination was shown in table 2 after a butterfly degree, drip-point of grease of each embodiment, shell roll (room temperature and 150 degrees Celsius, 24h), heat in 150 degrees Celsius. In addition, Additive such as oxidation inhibitor, anti-rust agent is added to grease of embodiment 6, and grease is made (example 1 2), the resultant which it was compared with commercial urea grease, and was examined was shown in table 3.

第 1 表

		比較例 1	比較例 2	比較例 3	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
(a)化合物	3,3'-ビトリレン-4,4'-ジイソシアネート g	7.97	8.09		6.56	4.86	2.73	4.91	4.9
	ステアリルアミン C ₁₈ g	16.03			13.22	9.78	5.50		
	オレイルアミン C ₁₈ g		15.91					9.65	9.6
(b)化合物	ジフェニルメタン-4,4'-ジイソシアネート g			11.80	2.08	4.60	7.75	4.64	4.6
	オクチルアミン C ₈ g			12.20	2.14	4.76	8.02	4.80	4.8
鉱油 g		176	176	176	176	176	176	176	
ポリオールエステル g									176
増ちょう剤含有量 %		12	12	12	12	12	12	12	12
(a)化合物/(b)化合物モル比		100/0	100/0	0/100	75/25	50/50	25/75	50/50	50/50
〔性状〕									
ちょう度 (25℃、混和)		273	276	265	268	269	265	273	284
滴点 °C		258	195	221	248	252	257	242	245
ジェルロール 24h	室温	>440	>440	283	348	344	333	356	362
	150℃	370	344	277	326	315	303	310	331
150℃加熱後ちょう度 (25℃、不混和)		148	136	185	157	168	174	163	164
音響試験 (120秒後)		32	32	51	18	21	23	19	21

表

2

第

	比較例 4	比較例 5	比較例 6	比較例 7	比較例 8	比較例 9	実施例 6	実施例 7	実施例 8	実施例 9	実施例 10	実施例 11
(c)化合物のジグリース	比較例 4 13.25	比較例 5 12.21	比較例 6 12.21	比較例 7 12.52	比較例 8 12.52	比較例 9 10.04	実施例 6 13.25	実施例 7 10.76	実施例 8 12.21	実施例 9 9.74	実施例 10 12.52	実施例 11 10.04
3,3'-ビトリレン 4,4'-ジイソ シアネート g												
2,4,2',6'(65% 35%)トリレンジ イソシアネート g		10.76		9.74		10.04		10.76		9.74		10.04
パラトルイジン g	10.75	13.24					10.75	13.24				
パラクロロアニ リン g			11.79	14.26					11.79	14.26		
メタキシリジン g					11.48	13.96					11.48	13.96
鉱油 g	176						176					
増ちょう割合含有量 %	12	12	12	12	12	12	12	12	12	12	12	12
実施例 8 のジウレアグリース / (c)化合物のジウレアグリース 重量比	0/100	0/100	0/100	0/100	0/100	0/100	80/20	80/20	80/20	80/20	80/20	80/20
〔性状〕												
ちゅう度 (25℃、提和)	363	372	386	395	346	380	280	285	287	288	277	286
滴点 °C	>260	>260	>260	>260	>260	>260	>260	>260	>260	>260	>260	>260
ジェルロール 24h 室温	405	>440	>440	>440	>440	>440	354	358	367	355	369	371
150℃	397	>440	>440	>440	>440	>440	317	327	341	343	336	349
150℃加熱後ちゅう度 (25℃、不混和)	160	181	107	218	53	181	172	178	159	188	151	180
音響試験 (120秒後)	157	272	231	642	258	555	15	20	26	22	25	19

第 3 表

項目	グリース	実施 例12	市販品A	市販 品B	市販 品C
ちょう度 (25°C、混和)		284	265	272	281
滴点 °C		>260	>260	242	249
ジェルロー ル 24h	室温	362	294	414	343
	150°C	327	253	>440	410
150°C加熱後ちょう 度 (25°C、不混和)		179	121	148	85
音響試験 (120秒後)		25	>10,000	2,020	150

測定法

ちょう度：JIS K2220

滴点：JIS K2220

ジェルロール：ASTM D1831

項目	グリース	実施 例12	市販品A	市販 品B	市販 品C
----	------	-----------	------	----------	----------

150°C加熱後ちょう度：JIS K2220に従い、1/4稠度

測定器にグリースを詰め、150°C、72h加熱後冷却

し、25°Cにおける不混和ちょう度を測定。

音響試験：特公昭53-2357号に記載の方法により

測定。

THIS PAGE BLANK (USPTO)